Polymer sorbent for mercury removal from aqueous solution

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Polymer sorbent for mercury removal from aqueous solution

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Abstract. The research study the feasibility of polysulfide sorbent (PSS) by using waste palm cooking oil and low-cost sulphur for mercury removal from aqueous solution. Mercury is known as one of the most hazardous toxic heavy metal that gives harmful to human being and environment. PSS is one of the materials that act as adsorbent to remove heavy metals. Waste palm cooking oil was used to produce PSS thus also can solved waste cooking oil management in Malaysia. The efficiency of PSS was investigated in this study based on the study of effect of initial Hg (II) concentration, contact time, pH and polymer sorbent dosage for removal of Hg (II) ion in aqueous solution. The characterization of surface morphology was examined by scanning electron microscopy (SEM). From this study, the highest mercury removal was 95.57 % at 120 rpm of agitation speed, 4 hour of contact time, initial Hg (II) ion concentration of 1 mg/L, 2 g of sorbent dosage and pH 6.

1. Introduction

Nowdays, the quality of the basic things in life called water is getting worse due to the presence of undesired chemical substances generate from various industrial activities without proper wastewater management. The contamination occurred due to the improper waste management in industry such as fabric, coal, food, leather, pharmaceutical, and colour industry, pesticides in agriculture, forestry and aquaculture drugs, and municipal wastewater, and also global changes gives huge effect to population [1]. Heavy metal pollutants become more noticeable compared to the wastewater pollutants when it is exposed to the surrounding. Most of the wastewater contain heavy metal that are present as persistent and non-biodegradable materials [2].

One of the most hazardous toxic heavy metal is mercury if it is not retained at a proper physiological concentration that harmful to human being. At high concentrations, mercury vapour inhalation can leads to death from respiratory failure. Long term exposure to mercury vapor primarily affects the central nervous system. Mercury also accumulates in kidney tissues, directly causing renal toxicity, and including proteinuria. Increasing of mercury concentration can cause damage of pulmonary function and kidney, chest pain and dyspnea [3]. Thus, an effective method must be introduced in order to remove mercury heavy metal to protect environmental safety and health.

Various wastewater treatment methods have been developed to remove heavy metal. These methods are oxidation, reduction, precipitation, ion exchange, membrane filtration, solvent extraction, and adsorption [4]. However, a few methods such as precipitation, ion exchange, and solvent extraction have

several drawbacks although it is used widely in industrial applications. The disadvantages of these methods are high cost, releases of toxics solvent, and disposal of sludge. The most favourable method is by using adsorption method due to its economic and technical for heavy metal removal in aqueous solution [5].

The adsorption method is very easy operation and convenient with a wide range of adsorbents used during adsorption process [6]. Cost effectiveness, high competence, and environmentally friendly compatibility are the reasons the adsorption treatment has gained much consideration. The adsorption efficiency is definitely reliant on the adsorbent properties and the adsorbent produced based on industry is sustainable, low cost and comparative in environment, therefore it looks to be vigorous for the removal of metal ions [7].

In this research, inexpensive polysulfide sorbent made from cooking oil waste derived from palm oil and sulphur from by-product of petroleum refining will be produce to treat the mercury heavy metal. Because sulphur is a by-product of the petroleum industry and recycled cooking oil will be a suitable starting material, the novel polymer can be made entirely from repurposed waste. This research is preparing sulphur polymers with sustainable and low-cost cross-linkers. The synthesis required a single, operationally simple chemical reaction. No purification was required and the transformation featured complete atom economy [8].

The reaction mixture appears as two transparent liquid phases. The sulphur appears orange or red on the bottom phase, while the yellow cooking oil resides in the top phase. Thermal homolysis of S-S bonds in elemental sulphur under these conditions generates thiyl radicals that initiate ring-opening polymerization of sulphur. The thiyl radical end groups contained in the resulting polysulfide intermediates also react with the alkenes of the cooking oil to form a cross-linked polysulfide. As this copolymerization occurs, the reaction mixture gradually becomes opaque and appears as one phase [9].

Elemental sulphur is a readily available and inexpensive material produced in excess of 50 million tonnes each year as a by-product of petroleum refining. Elemental sulphur can capture and stabilise mercury, but it suffers from several chemical and physical limitations that make it inconvenient to use directly in remediation [8]. Large amount of waste cooking oil are generated worldwide and this amount are varied depending on the amount of cooking oil consumed. Estimated about 15 million tons of waste cooking oil are generated worldwide [10].

Palm oil is the most used cooking oils worldwide. The palm oil industry is a major source of income for many people in the rural areas of many developing countries. Most of the production (84%) occurs in South East Asia, and most of the palm oil (84–90%) is used in food preparation [11]. In this study, by introducing low-cost mercury sorbents made uniquely from sulphur and unsaturated cooking oils are suitable starting materials, these mercury-capturing polymers can be synthesised entirely from waste.

The objective of this study is to evaluate the adsorption of mercury ion by PSS from aqueous solution by using one factor at one time (OFAT). The effects of initial concentration of mercury ion, contact time, pH and sorbent dosage of PSS were investigated under batch experimental conditions.

2. Materials and methods

2.1. Materials

The materials that involved in this research experiment were standard solution of mercury and sulphur that purchased from Merck. The waste cooking oil was collected from café and de-ionized water laboratory.

2.2. Preparation of polymer sorbent

The sulphur melted and heated up to 180°C. An equal amount of cooking oil was added slowly and the solution stirred rapidly. After 10 minutes of reaction time, a solid rubber formed. The experiment was using ratio 50 to 50 sulphur added to cooking oil (50:50) to produce polymer sorbent named polysulfide. Polymer sorbent produced was soaked with 0.1M NaOH in order to remove impurities. Then, the

polymer sorbent was milled in a blender to give particles less than 12mm in diameter and sieved at 0.5 mm.

2.3. Characterization of polymer sorbent

The sorbent surface morphology was observed by using surface electron microscopy (SEM). The surface morphology of polymer sorbent using waste cooking oil before and after adsorption study was analyzed in details. Scanning electron microscopy was conducted using JOEL-JSM-7800F model. This model was piloted at 5000× magnification.

2.4. Mercury removal from simulated wastewater

Adsorption studies were carried out in 500 mL beaker and the total volume of the reaction mixture was kept at 250 mL. The study was carried out by using jar test at room temperature to represent the environmentally relevant condition. After equilibration, this sorbent solution mixture was shaken on at a constant speed of 120 rpm for 4 hour. At the end of each experiment, the content of beaker was filtered using a Whatman No. 101 filter paper after which the concentration of residual Hg (II) ions in each filtrate was determined. The effect of sorbent dosage was carried out by adding different amounts of sorbent dosage ranging from 1 to 7 g to 250 mL of 5 mg/L of Hg (II) ions solution. The effect of contact time on Hg (II) ions adsorption was investigated by agitating 2.0 g of polysulfide sorbent and 250 mL of 5 mg/L of mercury solutions. The sample was shaken at 120 rpm for 5 hour. Every 30 minutes the sample was taken until 5 hour. The effect of initial concentration of Hg (II) ions was conducted by agitating 2.0 g in 250 mL of 1 mg/L of Hg (II) ions solution. The step then was repeated using 1, 2, 3, 4, 5 and 6 mg/L of Hg (II) ions solution. The effect of pH on Hg (II) ions adsorption was studied by agitating 2.0 g of PSS and a series of 250 mL Hg (II) solution with the concentration of 5 mg/L at different pH values, ranging from pH 1 to 7. Hydrochloric acid (HCl) and sodium hydroxide (NaOH), both 1.0 M, was used to adjust the pH of Hg (II) ions solution to the desired value prior to experiment.

2.5. Simulated wastewater

One hundred milliliter of 1000 mg/L of mercury standard solution purchased from Merck. After that, this solution was undergo dilution process to required concentration in ppm (mg/L) of mercury solution by using the formula of $M_1V_1 = M_2V_2$.

2.6. Percentage mercury removal measurement

After the adsorption process, the concentration of mercury solutions was determined using mercury analyser to analysis the performance of polysulfide sorbent to remove mercury heavy metal. The amount of adsorption, q_e (mg/g) and the percentage of mercury removal, R are calculated by using equation 1 and 2 below [12].

$$q_e = \frac{(C_o - C_e)V}{M_m} \quad (1)$$

$$R\ (\%) = \frac{C_o - C_e}{C_o} \times 100\ \% \quad (2)$$

Where, q_e is adsorption capacity (mg/g) at equilibrium, C_0 is initial mercury concentration (mg/L), C_e is equilibrium concentrations (mg/L) of the mercury solution, V is the volume (L) of mercury solution used, and M_m is the mass (g) of polysulfide sorbent used for adsorption test.

2.7. Mercury analyser

The samples were analyzed using Mercury Analyser RA-3310 (Nippon Instrument Corporation, Japan) that was available in Faculty of Chemical Engineering and Natural Recourses laboratory of Universiti Malaysia Pahang. This model applied the reducing vaporization mercury analyser. The benefits of this model are ultra-high sensitivity with reduced sample volume, touch panel provides ease of operation and novel idea allows horizontal or vertical configuration. In addition, it provides the Quality Assurance standard during measurements. The value of the result was present in the form of metal uptakes and amount of metal ions adsorbed.

3. Results and discussions

3.1. Characterization of the adsorbent

The surface morphology of PSS (ratio 50:50, waste) was analyzed by scanning electron microscopy (SEM) at 5000 magnification. Figure 1(a) (b) shows the surface morphology of PSS produced before after adsorption with mercury. The texture of PSS that produced from inverse vulcanization process is shown. Based on Figure 4.2(a), PSS present a locally smooth surface yet a high level of micro scale features that imparted high surface area. Figure 1(b) showed the surface of PSS changed after the adsorption indicated the presence of mercury-rich nanoparticles. The similar surface morphology for PSS by using canola oil reported by [8] which is micro texture that indicated high surface area.

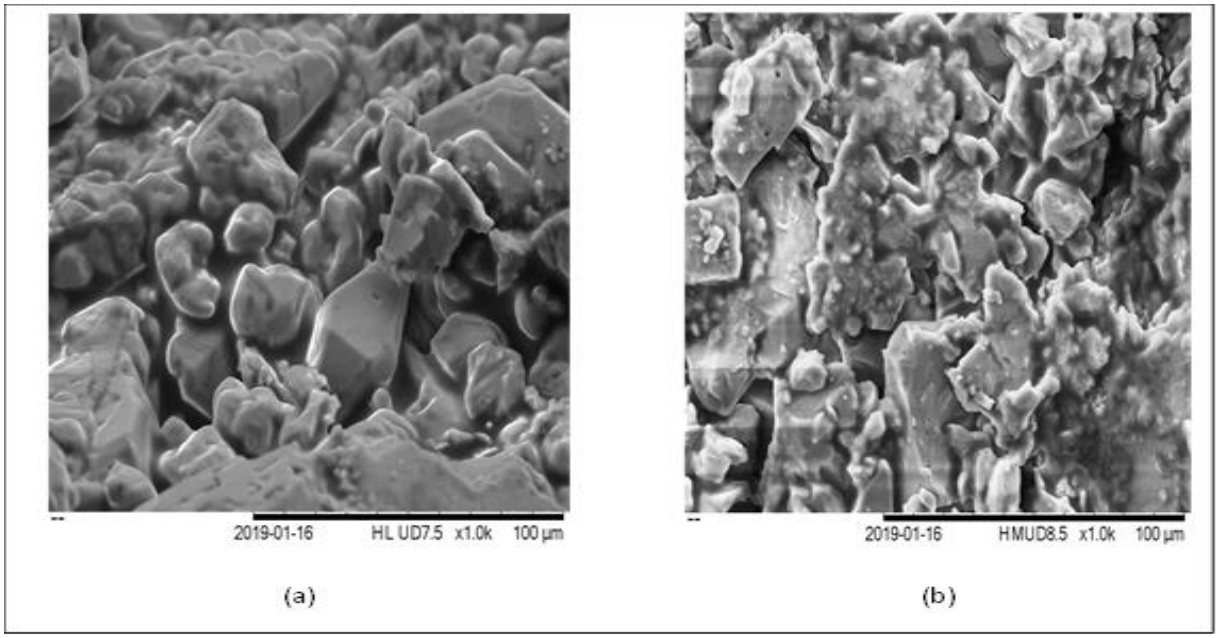

Figure 1. Surface morphology image of polymer sorbent using waste cooking oil (a) before adsorption with mercury, (b) After adsorption with mercury.

3.2. The effects of initial Hg (II) ion concentration

Figure 2 presented the effect of initial Hg (II) ion concentration on its adsorption in the range of 1 - 6 mg/L into the polymer sorbent. The percentage removal of Hg (II) ion from aqueous solution increase significantly with the reduction in the initial concentration of Hg (II) ions in the solution because the amount of polymer sorbent used was fixed in this study. In this experiment, the highest percentage removal of Hg (II) ions was 95.57% at the initial Hg (II) ion concentration of 1 mg/L. The adsorption efficiency decrease from 95.57% to 76.67% as the concentration of Hg (II) ions was increase from 1 to 6 mg/L. When all the active sites are involved in the adsorption process, the saturation and the maximum adsorbent capacity is achieved.

According to [13] similar trend has been reported where at low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the ions were easily adsorbed and removed. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of ions. The increased q_e higher initial concentration can be attributed to enhanced driving force.

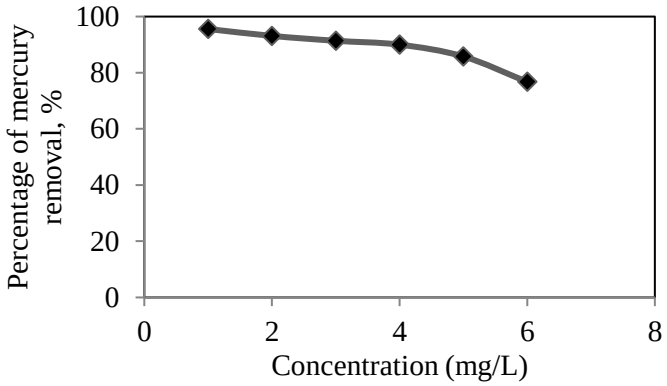

Figure 2. Effect of initial concentration on Hg (II) removal.

3.3. The effect of contact time

The effect of contact time on the adsorption of Hg (II) ion is shown in Figure 3. The adsorption of Hg (II) onto polymer sorbent increased with the increasing contact time. It can be observed that the adsorption of Hg (II) ion removal was very fast with time from 0 to 60 min. The trend is reported similar with (Sangu et al., 2015), where the adsorption consists of two phases: a primary rapid phase and a second slow phase.

The contact time needed for Hg (II) ion solutions to reach equilibrium was 60 min and reached a plateau at 60 - 240 min with 86.62 % of Hg (II) ion is adsorbed. According to [14] such rapid adsorption is because of great number of various functional group and also high specific area. Also, this could be reasonably attributed to the absence of internal diffusion resistance. Then, when the remaining functional sites decreases, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the polymer sorbent surface and in the liquid phase of Hg (II). It is reported that [15] shows the same general trend that then decreased gradually while approaching the equilibrium.

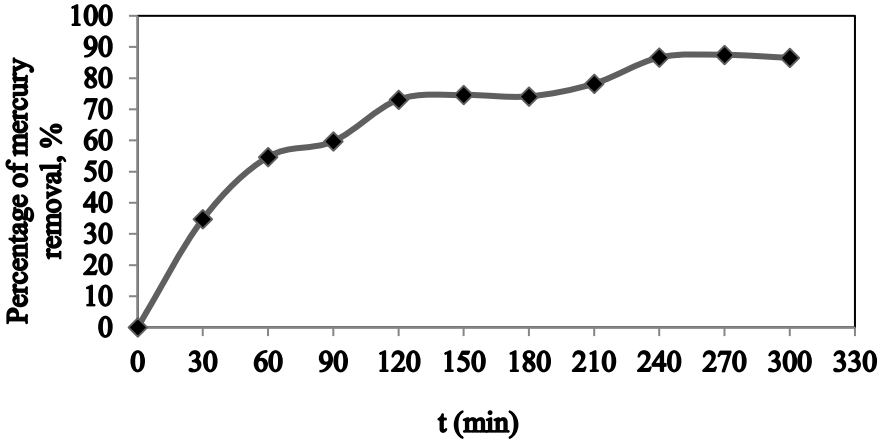

Figure 3. Effect of contact time on Hg (II) removal.

3.4. The effect of polymer sorbent dosage

The effect of polymer sorbent dosage on the adsorption of Hg (II) ions using PSS from waste cooking oil is shown in Figure 4. The increase in the sorbent dosage from 1 to 7 g gradually increased the percentage removal of Hg (II) ions from the aqueous solution. From the result, increasing the adsorbent dosage from 1 to 7 g, the adsorption efficiency increased from 74.46% to 94.77%.

According to [16] the dosage of adsorbent was a key parameter to control both availability and accessibility of adsorption higher dosage of adsorbent will increase the adsorption due to more surfaces and functional groups are available on adsorbent on which metals could interact with. These chemical groups were important in the formation of Van der Waals bonding as the functional groups played the main role in binding metals to the adsorbent during adsorption process. This provided more possibilities for adsorption to occur since there was less competition between metals for the binding sites.

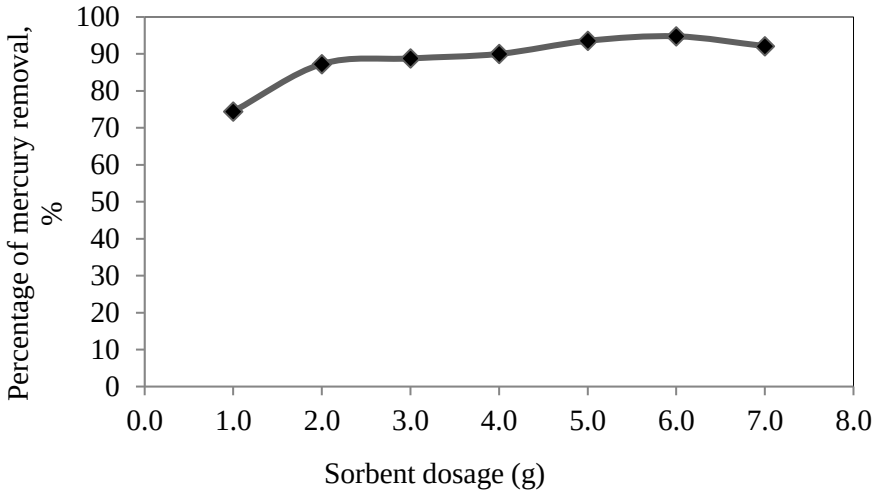

Figure 4. Effect of polymer sorbent on Hg (II) removal.

3.5. The effect of pH

The effect of pH on Hg (II) ions removal is shown in Figure 5. The data obtained from the adsorption of Hg (II) ions onto PSS show that the adsorption increased with the increase in pH from 1 to 5. At the highest acidity of pH 1, the Hg (II) ions removal was the lowest of only 53.24%. At pH 5, the Hg (II) ions removal was the highest which achieved until 88.61%.

The similar result was found for the adsorption of Hg (II) ion for new effective adsorbent named modified mesoporous silica (SBA-15) with trithiane, where [17] reported that , the percentage of Hg(II) ions adsorption increased significantly between pH 4.0 – 5.0 and then at pH higher than 5.0 decreased extremely. According to [18], at pH values below 2, hydrogen ions are likely to compete with mercuric ions and at pH values above 7 mercuric ions might precipitate. It is noticed that the adsorption decreased with the increase of pH value.

In fact, according to [19] higher pH values were avoided to prevent possible precipitation as hydroxides. The effect of pH can be explained in terms of electrostatic interactions initiated by the adsorbent. At lower pH, the surface charge of the adsorbent is positive which is similar to the predominant metal species in the solution. Therefore, the removal of metals in the pH range of 3–4 is low because of the less inclination of the metal species to migrate to the adsorbent because of like-charges repel. As the pH becomes less acidic (higher pH), there is a greater possibility for the positive metal ions to be attracted to increasingly negatively charged adsorbents. Moreover, there are also possible sites on carbonaceous surface for specific adsorption of H^+ ions that can be exchanged with the cation in the solution.

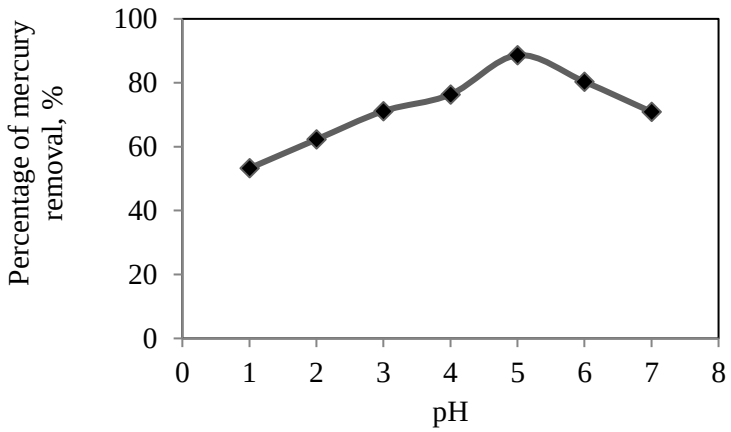

Figure 5. Effect of pH on Hg (II) removal.

4. Conclusion

In this study, the removal of Hg (II) ion from aqueous solutions using PSS was conducted using different effect of factor which were effect of initial Hg (II) ion concentration, polymer sorbent dosage, pH and contact time. The highest mercury removal was 95.57 % when the parameters were at 120 rpm of agitation speed, 4 hour of contact time, initial Hg (II) ion concentration of 1 mg/L, adsorbent dosage 2 g of adsorbent dosage and pH 6. Overall, it can be concluded that polysulfide sorbent has the potential to be used as a suitable polymer sorbent for the removal of mercury from aqueous solution thus solve the waste cooking oil management in Malaysia.

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